Molecular Dynamics Simulation on Specific Heat of Undercooled Fe-Ni Melts

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ABSTRACT: In this paper, a Molecular Dynamics Simulation based on EAM (embedded atom method) is applied to calculate the specific heat capacity of Fe-33%Ni alloy at temperatures above and below the melting temperature. The relationship between the specific heat of the alloy and the undercooling is investigated. The heat capacity of Fe-Ni alloy fixed at a constant value in the superheated and undercooled liquid states. A comparison between previous and current studies of the authors shows that the heat capacity behaviors of undercooled alloy strongly depends on the species of the alloy.

Keywords: Fe-Ni alloy, Molecular dynamics simulation, EAM, heat capacity, undercooled

1. INTRODUCTION

Knowledge of the thermodynamic properties of the undercooled liquid is necessary to characterize this metastable state and to describe the solidification behavior of undercooled melts. In particular, specific heats are of interest because knowledge of specific heat of the undercooled liquid can give some information about the speed of crystal growth[1], short-range order of liquids[2], nucleation rate[3] and the ideal glass transition temperature[4]. However, there are few experimental data about the specific heat capacities of the undercooled melts, especially about high-melting-point metals. This is because that it is difficult to avoid the crystallization of the undercooled melts on a time scale, which allows for calorimetric investigations. As a result, the demand of developing reliable predictive methods has never been weakened.

The molecular dynamics simulation (MDS) is a powerful method developed in the past decades. It has been widely used in materials science. With the development of capability of computer, the atomic-scale simulation has proven to be an effective method in understanding materials' preparation process and predicting the thermophysical properties in some extreme cases. Fe-Ni alloy is widely used as a corrosion-resistant material, which has higher initial and maximum permeability than silicon iron. However, there is a lack of experimental data of Fe-Ni alloy heat capacities, especially in the undercooled region. The main purpose of this paper is to investigate the specific heat of Fe-33%Ni alloy by MDS.

2. EMBEDDED ATOM METHOD

The embedded-atom method (EAM) is one of the distinguished potential which gain great success in describing the interaction of particles of metals and alloys. It has been shown to give good results in simulations of reconstructions, thermal expansion, surface and liquid structure and even the undercooled liquid-to-glass and liquid-to-crystalline transitions.

The embedded-atom method is a procedure for designing a mathematical model of a metal, which was developed by researches at Sandia National Laboratory[5,6]. The basic equations of the embedded-atom method are[6]:

$$E_{tot} = \sum_i F_i(r_i) + \frac{1}{2}\sum_{i,j(i\neq j)} f_{ij}(R_{ij}) \quad (1)$$

$$r_i = \sum_{i\neq j} f_j(R_{ij}) \quad (2)$$

Where E_{tot} is the total internal energy, r_i is the electron density at atom i due to all other atoms, f_j is the electron density of atom j as a function of distance from its center, $R_{i,j}$ is the separation distance between atoms i and j, $F_i(r_i)$ is the energy to embed atom i in an electron density r_i , and $f_{i,j}$ is a two-body central potential between atoms i and j. In this paper, an analytic nearest-neighbor model, which was developed by Johnson [7,8], was adopted. For iron, the embedded energy is shown as follow.

$$F(\rho) = -(E_C - E_{1f})\left(1-\gamma\ln\left(\frac{\rho}{\rho_e}\right)\right)\left(\frac{\rho}{\rho_e}\right)^{\gamma} \quad (3)$$

$$f(r) = f_e(r_{1e}/r)^{\beta} \quad (4)$$

For nickel, the embedded energy is shown as follow[8].

$$F(\rho) = -E_c\left[1-\gamma\ln\left(\frac{\rho}{\rho_e}\right)\right]\left[\frac{\rho}{\rho_e}\right]^{\gamma} - \Phi_e\left[\frac{\rho}{\rho_e}\right]^{\gamma} \quad (5)$$

For iron, the monatomic pair potential is as follow:

$$\phi(r) = k_3\left(\frac{r}{r_{1e}}-1\right)^3 + k_2\left(\frac{r}{r_{1e}}-1\right)^2 + k_1\left(\frac{r}{r_{1e}}-1\right) + k_0 \quad (5)$$

For Nickle, the monatomic pair potential is as follow[8]:

$$\phi(r) = \phi_e \exp\left(\gamma\left(\frac{r}{r_{1e}}-1\right)\right) \quad (6)$$

Since the electron density at any location is taken as a linear superposition of atomic electron densities, and the embedding energy is assumed to independent of the source of the electron density, these two functions can be taken directly from monatomic models. For two different types of atoms (a-type and b-type), the pair interaction is modeled as[8]

$$\phi^{ab}(r) = \frac{1}{2}\left(\frac{f^b(r)}{f^a(r)}\phi^{aa}(r) + \frac{f^a(r)}{f^b(r)}\phi^{bb}(r)\right) \quad (7)$$

The superscripts a and b indicate the a- and the b- type atoms in a binary alloy. $\phi^{aa}(r)$ and $\phi^{bb}(r)$ are the monatomic potentials which could be given by the monatomic models.

3. SIMULATION DETAILS

Usually, there are two kinds of statistic method in calculating the specific heat. The first one is to derive the specific heat from the fluctuation of energy[9].

$$C_v = \frac{\left\langle dE^2 \right\rangle_{NVT}}{K_B T^2} \tag{8}$$

The second one is to determine the specific heat from the differential of the enthalpy function of temperature:

$$C_v = \frac{dE(t)}{dt} \tag{9}$$

Considering the ability of the computer system, 500 molecules were simulated. Since there are only 500 molecules in our simulation system, the calculation of Cv via fluctuation is not stable. So, in this paper, the second method is adopted.

At the beginning of the simulation, 334 iron and 166 nickel atoms were arranged in face-centered cubic box subject to periodic boundary conditions. The time step was 5.0×10^{-15} s. In order to get an equilibrium liquid state in the simulation, the system started at 2100K which is above the melting point. This temperature was kept constant for 500,000 steps. Then the quenching process with the cooling rate of $4\times10^{11}\,\mathrm{Ks}^{-1}$ was carried out to calculate the internal energy E at 100 K intervals of temperature. At each temperature, 400,000 steps were carried out for relaxation. Then 100,000 more steps were taken to calculate the internal energy E. The simulation was ended up at 1200 K which is 533 K lower than the melting point. Since the quenching process is very fast, the copper keeps in undercooled liquid state. All the parameters used in the simulation are shown in Table1 and Table 2.

Table 1 The input parameters Ec and the model parameters f_e, f_e, a, b, g for nickel[8]

E_{1f} (eV)	E_c (eV)	f_e	f_e (eV)	a	b	g
1.6	4.45	0.41	0.74	4.98	6.41	8.86

Table 2 Model parameters for iron, k_i (I=0, 1, 2, 3) in $\mathrm{eV}/\mathrm{\AA}^o$, E_c, E_{1f} and a in eV[10]

a	E_c	E_{1f}	γ	f_e	k_3	k_2	k_1	k_0
2.866	4.29	1.79	0.37	0.36	-13.31	9.21	-0.88	-0.27

The simulated result of internal energy E is shown in Fig. 1. The energy has a linear relationship with the temperature. That means the heat capacity is fixed at $457\,\mathrm{J/Kg\cdot K}$ in the region between 1200K and 2100K, as shown in Fig. 2. The heat capacity of Fe-Ni alloy behaves differently as compaired with the heat capacity of Cu-Ni alloy[11]. The simulation results of heat capacity of Cu-25%Ni alloy behave a slightly decrease with the increase of temperature in the region from 1100K to 2000K, while increase with the increase of temperature in the region from 800 to 1100K (Shown as Fig. 3). The heat capacities of undercooled liquid metals are generally considered to be remarkably different from that of the liquid states above the melting point[12]. This agree with the simulation of Cu-Ni alloy. However, the Fe-Ni and Cu-Ni alloys are simulated with the same model, while the heat capacities' behaviors of the two alloys are quite different from each other. So, the behavior of the heat capacities of undercooled liquid alloys might be remarkably diffenrent, it strongly depends on the species of the alloy.

4. CONCLUDING REMARKS

The specific heat of a iron and nickel alloy, Fe-33%Ni, was simulated with a molecular dynamics simulation based on EAM.

The simulation obtains the specific heat of Fe-33%Ni, ranged from undercooled region to superheated region. The results show that the heat capacity of liquid Fe-33%Ni above and under melting point keeps in a fixed value. So, in the prediction of crystal growth and the nucleation rate, an average heat capacity is suitable.

The results also show that, although the heat capacity of undercooled liquid metal is generally thought to be different from that of the liquid metal above melting point, it is not the case for Fe-Ni alloy. The behaviors of heat capacities of alloys may strongly depend on the species of alloys.

Acknowledgement

This research is supported by National Natural Science Foundation of China under Grant No. 59876016, the Project of High Technology & Development program of China (863-3-2), the Fundamental Research Foundation of Tsinghua University under Grant No. Jc 1999038, the Doctoral Education Fund of Tsinghua University and the Tsinghua Tongfang high performance computational foundation.

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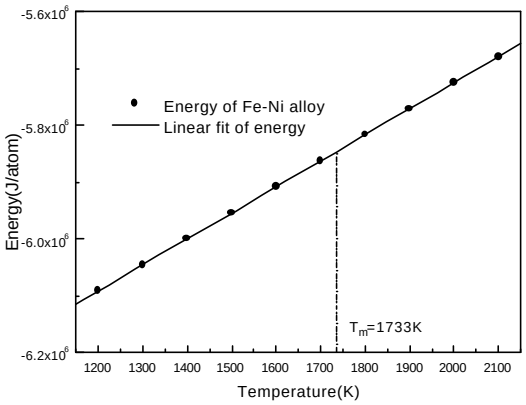

Fig. 1 The average internal energy of Fe-33%Ni

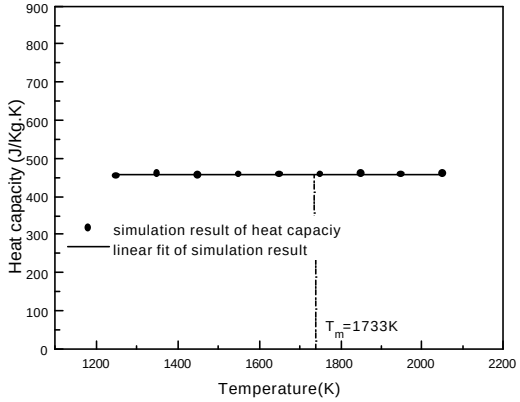

Fig. 2 The simulation result of heat capacity of Fe-33%Ni

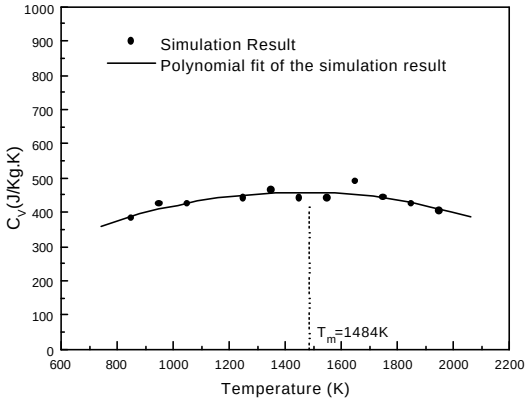

Fig. 3 The simulation result of heat capacity of Cu-25%Ni